

X-ray Photoelectron Spectroscopy as a Probe of Thin Dielectrics

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As dimensions in microelectronics shrink, new materials become important, and their interfaces with other materials play an important role in the performance of the device. One example of this is the dielectric materials used in capacitors for random access memories and as gate dielectrics for field effect transistors. In these applications, materials with higher dielectric constant permit physical dimensions to shrink and circuit speeds to increase. We have used x-ray photoelectron spectroscopy to study chemical defects in two of these materials, silicon oxynitride and tantalum pentoxide. These chemical defects are related to electrical defects. Angular dependence of photoelectron spectra permits determination of the distribution of nitrogen as a function of depth through the oxynitride film. In addition, the N 1s photoelectron spectrum has four components. By studying the adsorption of nitromethane on silicon, first principal calculations, near edge x-ray absorption spectroscopy, and electron-spin resonance experiments these components can be assigned to nitrogen bonded to two oxygen atoms and one silicon, nitrogen bonded to one oxygen and two silicon atoms, nitrogen bonded to three silicon atoms, and nitrogen bonded to two silicon atoms with one dangling bond. It is the presence of this dangling bond that acts as an electron trap in the oxynitride. In tantalum pentoxide it has been difficult to directly observe the chemical defects that act as electrical defects. By apply an electrical potential to tantalum oxide film and collecting the photoelectrons emitted through a thin Pt film, the potential distribution through the film can be determined. This measurement shows that the electrical defects are largely localized near the electrode interface. Through examples like these, we will show how chemical moieties can be related to the electrical properties of dielectric films.

Soft X-ray Absorption Spectroscopy at 25 nm Spatial Resolution

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Recent technical advances allow imaging with the XM-1 soft x-ray microscope with a spatial resolution of 25 nm and a spectral resolution of $E/dE = 700$. We report on both the technical advances which make this possible and some of the applications which can use these capabilities. The XM-1 is a full field imaging microscope which uses zone plates for both the condenser and objective elements and is located at the Advanced Light Source. The illumination energy can be tuned between 250 and 900 eV. The high resolution imaging capabilities are used in biology, materials science, and environmental science. Magnetic materials are imaged at high spatial resolution by x-ray magnetic circular dichroism. Element specific contributions to the magnetization can be obtained within a sample even in the presence of a capping layer. High contrast, high spatial resolution images at the L-edges of Fe and Co will be shown for magnetic storage material.

Photoelectron diffraction and holography: Present status and future directions

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The development and exploitation of photoelectron diffraction as a means of obtaining structural information about surfaces and ultra-thin films has grown considerably in the two decades or so since its original 'discovery', and the pace of this expansion appears to be growing. Three factors have contributed this, namely the availability of increasingly more and better synchrotron radiation beamlines, the appreciation of what can be achieved by the technique through a series of successful applications, and the novel attraction of structure determination through direct inversion of the experimental data, commonly referred to as 'holographic inversion'. In this brief review some of the strengths and dangers to be identified in work so far, and foreseeable future developments and applications will be presented.

Although the view of the process as photoelectron holography has attracted a great deal of interest, and there now appear to be a number of alternative theoretical approaches for inverting the data in a fashion which removes the most serious artefacts of the earliest schemes, it is important to recognise that such methods were only ever intended as a means of obtaining first-order approximate structures which can be tested and refined using more exact modelling. Such a first step is important in easing the problems of uniqueness which exist in pure trial-and-error methods, but should never be a substitute for proper quantitative structure analysis, now well-established using photoelectron diffraction. Nevertheless, the need for large data sets (in emission angle and energy) in order to remove many of the artefacts of 'holographic inversion' is a valuable improvement relative to quite a number of previously under-constrained structure 'determinations'. The holographic view of the process is of limited relevance to photoelectron diffraction conducted at high electron kinetic energies where zero-order (forward) scattering dominates, and simple first-order structural models can often be obtained by direct inspection of the raw data.

A key strength of photoelectron diffraction is the potential to obtain structural information in a fashion which is both element-specific and chemical-state-specific through the spectral fingerprint of the photoelectron core level binding energy. The increasing availability of undulator beamlines on third-generation synchrotron radiation sources offers the necessary combination of high photon flux and high spectral resolution needed to exploit this potential fully, and this seems likely to be a major growth area in the near future.

Suppression of the low-spin multiplet components in the 3p photoelectron spectra of atomic and solid 3d metals

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In recent years the 3p-photoelectron spectra of Cr, Mn, Fe and Co have been widely used to obtain information about the electronic and magnetic structure of metals, compounds, surfaces, thin films and multilayer systems. Especially spin-resolved photoemission and linear and circular dichroism in angle-resolved photoemission have proved to be powerful atom-specific probes. The interpretation of the experimental spectra has in most cases relied on atomic models, usually some variant of the independent electron model, while different schemes, e.g. cluster or ligand field models, have been used to take solid state effects into account. Due to the experimental difficulties there are only a few 3p-photoelectron spectra known of free atoms and ions compared to the situation for solids. The spectra of atomic Cr and Mn, metals which sublime at a relatively low temperature, were the first to be studied. The 3p-3d interaction in the final ionic state gives rise to an LS multiplet structure spanning a binding energy range of around 20 eV. Theoretically high-spin components at low binding energy contrast low-spin components at high binding energies. Experimentally strong lines at low binding energy contrast some weak structure at high energy but the experimental spectra published so far, in particular for metals, either suffer from insufficient energy resolution or they do not cover the full energy range. In order to determine the multiplet splitting as well as the strength and the width of the different components we studied the 3p-photoelectron spectra of Cr, Mn, Fe and Co atoms experimentally and theoretically. On this basis we hope to be able to provide a reliable basis for assessing the atomic effects in the solid state spectra. For comparison the 3p-photoelectron spectra of Cr and Mn metals were also measured.

Term dependent lifetime broadening by super-Coster-Kronig decays turns out to be the main cause of the almost complete suppression of the low-spin lines at high binding energy. The corresponding 3p-photoelectron spectra of the metals only display a single broad asymmetric line which we associate with the high-spin components in the atom. We notice the significance of this result for the interpretation of, for example, experiments involving dichroism of 3d-metals.

We emphasize the similarities but in particular the significant differences in the interpretation of the 3p- compared to the more well known 3s-photoelectron spectrum in these elements.

Image potential state lifetimes on transition metal fcc (111) surfaces

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We have investigated the dynamics of image potential states on the clean and oxygen covered Pt(111) surface with time resolved two photon photoemission spectroscopy. Fsec pulses of a Ti:sapphire laser system with a photon energy of 6 eV were generated to populate the image potential states. In a photoemission setup time delayed 3 eV pulses allowed us to probe the population dynamics. The first two image potential states of the Rydberg series were resolved with binding energies of 0.65 ± 0.05 eV for the $n=1$ state and 0.16 ± 0.05 eV for the $n=2$ state relative to the vacuum level. Their respective lifetimes were determined to 26 ± 7 fs and 62 ± 7 fs and reflect the different degree of localization in front of the surface. We performed calculations within the GW approximation of many body theory and found good agreement with the measurements.

The value of 26 fs for the lifetime of the first image potential state on Pt(111) is close to the value of 25 fs obtained for Pd(111) [1] despite of the different position inside the band gap. In Pd(111) and Ni(111), the image potential states lie closer to the center of the band gap. First time resolved measurements of the first image potential state on Ni(111) point to a reduced lifetime for the $n=1$ state. Since the sp-electronic structure is very similar for the three surfaces the observed phenomena are most likely related to the changing d-level occupation. This is also evidenced by a reduction of the image potential state lifetimes on the well ordered Pt(111)-p(2 x 2)-O surface. We will discuss this effect in the light of a rearrangement of d-like density of states near the Fermi level.

[1] A. Schaefer, I.L. Shumay, M. Wiets, M. Weinelt, Th. Fauster, E.V. Chulkov, V.M. Silkin, P.M. Echenique, submitted to Phys .Rev. B

Autoionization of Triply Excited Rydberg Series

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We have studied the Auger rates of triply-excited Rydberg series and compared to the more well known decay behaviour of doubly-excited series. The prototype of a doubly-excited Rydberg series is the $2nl'$ series in He which has been studied extensively since the sixties. Non-radiative decay rates in such series generally decrease with n , roughly as n^{-3} . More recently triply-excited states have become accessible to experimental studies and the first observation of triply-excited Rydberg series has been reported [1]. This has prompted us to consider the decay patterns of such series. It turns out that there are three contributions to the total decay rate for such series since the electrostatic interaction, which is the cause of the decay, is a two-electron interaction and thus each of the three electrons can be a spectator to the decay of the two others. Consider the $2l2l'nl''$ Rydberg series as an example. Two of the contributions has one of the $n=2$ electrons as spectator and thus involve the nl'' electron in the decay. These decay rates decrease with n in the same way as for the doubly-excited series but the third possibility has the nl'' electron as spectator and this contribution, from the decay $2l2l'$ to $1skl''$, is nearly independent of n since only the free electron energy k will vary, slightly, with n . Thus we predict [2] that the decay rates of such series should be roughly independent of n . This very simplistic analysis turns out to be able to survive many-electron effects such as configuration interaction and lack of orthogonality between initial and final states, in particular for the $2l2l'nl''$ states. This result has consequences for example for the experimental detection of triply-excited Rydberg series as we will discuss at the conference.

[1] S. Diehl et al, Phys. Rev. Lett. 79, 1241 (1997)

[2] G. Verbockhaven and J.E. Hansen, Phys. Rev. Lett. 84, 2810 (2000)

Sub-Picosecond Pump and Probe Photoemission from Metals

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Bulk polycrystalline Cu and Mo samples with polished and prepared surfaces are excited by 100 fs laser pulses from an amplified Ti:Sapphire laser system. A Mach-Zehnder interferometer produces two collinear and orthogonally polarized beams with a controlled delay scan between pulses. In this way, high order correlations of the laser pulses are produced scanning simultaneously the photocurrent and the second harmonic generation in a BBO crystal. The correlation traces obtained from Cu and Mo samples have distinct characteristics: the peak to background contrast ratio and the FWHM of the correlation traces are different and clearly discriminate the photoemission properties of the metals. An explanation of the data is proposed, based on the different electronic band structure of the two metals.

Characteristics of the project of the new Beamline for Advanced diCHroic (BACH) at ELETTRA

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The new Beamline for Advanced diCHroism (BACH) is under construction at the ELETTRA Synchrotron Radiation Source in Trieste - Italy and is scheduled for commissioning is scheduled for the early fall 2000. The scientific case of the beamline is represented by light polarization dependent electron (x- ray absorption and photoemission) as well as photon (inelastic X-ray scattering) spectroscopy. X-ray photons in the 35-1500 eV energy range will be delivered by two Apple II elliptical undulators with full tunability of the light polarization and with polarization rates close to 100%. The beamline monochromator is based on the Padmore VASGM (Variable Angle Spherical Grating Monochromator) design. Three interchangeable spherical gratings will provide resolving powers of 20000-6000, 20000-6000 and 15000-5000 in the energy ranges 35-160eV, 200-500eV and 500-1500eV respectively. The photon flux in the experimental chamber has been estimated to be above 10¹¹ photons/s with linearly or circularly polarized light at the best resolution achievable with each grating. A fourth grating will be available to cover the 400-1600eV photon energy range with lower resolving power (10000-2000) but greater flux (10¹² photons/s) on the sample, for low counting rate experiments such as fluorescence and X-ray scattering experiments. The monochromatic beam can be deviated in either of two separate branches each one corresponding to an independent experimental station. Each branch contains a Kirkpatrick-Baez refocusing section based on plane elliptical mirrors that provide a nearly free-aberration spot on the sample, with 200'10mm² horizontal'vertical dimensions.

The detailed project of the beamline is presented, reporting the characteristics of the optical elements as well as the optical performances (monochromator's resolving powers and efficiencies, flux and spot dimensions).

Recording of X-ray Holograms on a Position Sensitive Detector

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In 1986, A Szöke proposed to use the atoms as sources of fluorescence x rays, photoelectrons or Auger electrons for holographic imaging of the surrounding of the emitter [1]. In contrast to the electron-emission holography, only a few demonstration experiments using x rays as hologram forming waves were carried out up to now, e. g. [2,3]. The small atomic scattering factor of x rays and low signal-to-noise ratio make difficult to detect fluorescence photons with sufficient statistics.

In all of the previous experiments, a narrow energy window around an emitter fluorescence line was realized by means of an energy dispersive detector [3] and/or a graphite crystal analyzer [2]. The drawback of these setups is the strong reduction of the photon count rate. Very recently, we have carried out a holography experiment by using an absorption filter in front of a detector without energy resolution. In this way we were able to increase the photon count rate by more than one order of magnitude [4].

We achieved further essential improvement by using an absorption filter in combination with a position sensitive detector [5]. The simultaneous recording of the whole hologram simplified the experiment as compared to the configurations used so far. The increase of the flux of detected fluorescence photons by more than two orders of magnitude reduced drastically exposure times. Moreover, high angular resolution and very precise detection of intensities made possible to reconstruct images of more distant atoms and/or images of weaker scatterers. The hologram of a GaAs monocrystal was recorded on an imaging plate and the images of atoms located up to more than 12 Å far from the emitter were obtained.

[1] A. Szöke, in Short Wavelength Coherent Radiation: Generation and Applications, edited by T. Attwood and J. Boker, AIP Conference Proceedings No. 147 (AIP, New York, 1986).

[2] M. Tegze and G. Faigel, Nature (London) 380, 49 (1996).

[3] T. Gog, P. M. Len, G. Materlik, D. Bahr, C. S. Fadley, and C. Sanchez-Hanke, Phys. Rev. Lett. 76, 3132 (1996)

[4] E. Busetto, M. Kopecky, A. Lausi, R. H. Menk, M. Miculin, and A. Savoia, Phys. Rev. B (to be published).

[5] M. Kopecky, E. Busetto, A. Lausi, M. Miculin, and A. Savoia, Phys. Rev. Lett. (submitted for publication).

Recent ARPES results on Bi₂Sr₂CaCu₂O₈ - Fermi surface and anomalous dispersion

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High resolution Angle Resolved Photoemission data from pure and Pb doped Bi₂212 is presented. Data with very high resolution and significantly higher momentum space sampling of three Brillouin zones unambiguously demonstrates the presence of the large electron-like Fermi surface in Pb-doped compound. Several complementary methods for determining the Fermi surface are applied yielding the same result. Implications for pure Bi₂212 are discussed. The anomalous dispersion behavior is observed in all the samples, providing strong evidence of electron interactions with a collective mode.

Extracting the Self Energy from the Spectral Function of the High Tc Superconductors

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We have earlier shown [1] that, under suitable experimental conditions, the impulse approximation holds, and ARPES measures the spectral function. Here we show how the changes in the real and imaginary parts of the self energy can be extracted from ARPES data without any modeling or background subtraction. We use this technique to show that superconductivity introduces a new energy scale in the electronic structure of the marginal normal state of the high temperature superconductors. We further find that this energy scale manifests itself throughout the Brillouin zone, and direct comparison of ARPES to neutron spectroscopy on the same samples indicates that this energy scale arises from the interaction of electrons with a bosonic collective mode.

Spin-resolved photoemission and XAS studies on half-metallic ferromagnetic oxides

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I present electron spectroscopic results on half-metallic ferromagnetic oxides, doped manganites and chromium dioxides. In the study of the doped manganite, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, the half-metallicity was investigated by using the spin-resolved photoemission spectroscopy. Well below the Curie temperature, T_C , the results clearly manifest the half-metallic nature, i.e. for the majority spin, the photoemission spectrum shows a metallic Fermi cut-off, whereas for the minority spin, it shows an insulating gap. On heating through T_C , the spectrum shows no difference for different spins and the spectral weight at E_F disappears, indicating that the Mn 3d spins become disordered and the system undergoes the ferromagnetic metal to paramagnetic non-metal transition. The magnetism for three different length scales were obtained from superconducting quantum interference device (SQUID), soft x-ray absorption magnetic circular dichroism (XMCD), and spin-resolved photoemission (SRPES) measurements. In the study on chromium dioxide, CrO_2 , which is well known to be half-metallic, the orbital anisotropy was investigated by using the polarized x-ray absorption spectroscopy. The results show that the orbital occupation of CrO_2 ($3d^2$) exhibits a strong anisotropy.

Electronic Structure Study of PtSi by Synchrotron Radiation Photoelectron Spectroscopy*.

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Among its low barrier Schottky contact or the special interest in the novel PtSi-n-Si Schottky photodiode, the Platinum Silicide (Self-Aligned-Silicide) maintain stable electrical and mechanical integrity with reduced vertical and lateral dimensions, thus showing potential for applications in the next generation of ULSI. On the other hand, a strong correlation between the quality of the silicide and the presence of contaminants (mainly oxygen) during the silicide formation has been previously reported. Today, and despite its technological and scientific interest, the electronic and atomic structure of the platinum silicide (PtSi) polycrystalline epitaxial growth on Si surface has only been fairly studied. We present valence band and core level synchrotron radiation photoelectron spectroscopy studies on Pt growth on clean Si(100) and the resulting new species formed after annealing. In addition we also show changes in the electronic structure motivated by the presence of oxygen and at different stages of the silicide formation. We also propose a new explanation for the kinetic process of the oxygen interdiffusion and its time and temperature dependence in the annealing procedure. Finally, PtSi samples prepared by ZAE-BAYERN laboratories were also characterized by Photoelectron Spectroscopy (PES) and X-Ray Absorption Spectroscopy (XAS). These results were compared to the in-situ prepared PtSi.

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Two-Component Electronic Structure in the Stripe Phase and High Temperature Superconductors

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We have carried out high resolution angle-resolved photoemission spectroscopy measurements on $(\text{La}_{1-4-x}\text{Nd}_{0.6}\text{Sr}_x)\text{CuO}_4$ (Nd-LSCO) ($x=0.10, 0.12$, and 0.15), a model system of static stripe phase, and $(\text{La}_{2-x}\text{Sr}_x)\text{CuO}_4$ (LSCO) ($x=0.5\sim 0.22$), high temperature superconductors with possible dynamic stripes. We have observed that the stripe phase exhibits two-component electronic structure. On the one hand, it shows one-dimensional electronic structure with the frequency integrated spectral weight confined inside one-dimensional segments in the momentum space (defined by $|k_x|=p/4$ and $|k_y|=p/4$); the low energy excitation is confined near $(p, 0)$ and $(0, p)$. On the other hand, it shows two-dimensional Fermi surface which contains nodal spectral weight. These findings point to a possible coexistence of site- and bond-centered stripes in the system.

Photoionization of Singly-Charged Positive Ions Using Synchrotron Radiation

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A new photoion-yield spectroscopy apparatus has been developed in order to study the electronic structure of atomic and molecular ions. This accelerator-based apparatus takes advantage of the merged-beams method, where a fast-moving ion beam is brought onto a common axis with a counter-propagating energy-resolved photon beam. Photoions produced along the merge-path are separated from the target ion beam in a uniform magnetic field, and ion-yields are monitored with a charged-particle sensitive detector. The apparatus is capable of making absolute measurements of photoionization cross- sections along isoelectronic and isonuclear sequences of positive ions. Recent results of high-resolution measurements for the photoionization of Ne^+ and other beams of singly-charged positive ions will be presented.

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CORROSION BEHAVIOUR OF THE 6063-T5-ALUMINIUM COATED WITH POLYPYRROLE

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The 6063-T5-aluminum alloy is widely used in the heat-exchanger industry. The mechanism of action of the inhibiting anions on the corrosion of aluminum in a near-neutral solution involves the following steps:

- Reduction of the dissolution rate of the passivating oxide film
- Repair of the oxide film by promotion of the reformation of oxide
- Repair of the oxide film by plugging pores and coat the surface by insoluble compounds
- Prevention of the adsorption of aggressive anions.

When aluminium is immersed in water, the air formed oxide film of amorphous γ -alumina initially thickens (at a faster rate than in air) and then an outer layer of crystalline hydrated alumina forms, which eventually tends to stifle the reaction. It is well-known that the inhibition of aluminum corrosion occurs only when the initial rate of dissolution of aluminum oxide in solutions of anions is smaller than a critical value. Among the various protective coatings, polymer coatings of aluminum is of great industrial interest. In this connection we have investigated the corrosion behaviour of polypyrrole coated aluminium using (I) Electrochemical (Polarisation Curves and Electrochemical Impedance Spectroscopy), (II) Spectroscopic (X-ray Photoelectron Spectroscopy), and (III) Microscopic (Scanning Electron Microscopy) methods in a chloride containing solutions and at different pH values. A substantial inhibition effect is observed for the polymer coated aluminium electrodes. Electrochemical and Spectroscopic findings and various experimental parameters, like the influence of the polymer deposition condition on the corrosion of aluminum, will be presented.

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NEXAFS Spectra of Metallotetraphenylporphyrins with Adsorbed Nitrogen Monoxide

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The electronic structures of metallotetraphenylporphyrins (MTPPs : $M=\text{Co}(\ddot{\text{O}}^+)$, $\text{Cr}(\ddot{\text{O}}^\circ)$, $\text{Zn}(\ddot{\text{O}}^+)$, and $\text{Ru}(\ddot{\text{O}}^+)$) with and without adsorbed nitrogen monoxide (NO) were studied by near edge X-ray absorption fine structure (NEXAFS) spectroscopy. These materials have attracted interest do to their electron donor-accepter properties and related applications to some electronic devices e.g. gas sensor. The nitrogen (N) K-edge NEXAFS spectra were measured in the total electron yield mode at BL-11A of Photon Factory. The spectra obtained from MTPPs before NO adsorption were similar to each other, and three $\text{N}1s \rightarrow \pi^*$ transitions were observed at low photon energy side. These peaks were assigned to π^* (eg) (~ 399 eV), π^* (b_{2u} , eg) (~ 401 eV), and π^* (a_{2u}) (~ 404 eV) from low photon energy side [1]. After NO adsorption on MTPPs, N K-edge NEXAFS spectra were changed. In the case of CoTPP and RuTPP, a new peak was observed at 403.5 eV. Furthermore, the peak around 401 eV disappeared for CoTPP. For CrTPP and ZnTPP, two new peaks were observed at 403.5 eV and 405.3 eV. We consider that these differences are due to the difference in the number of d electrons in transition metals. Based on these results, the adsorbed states and electronic states of NO on MTPPs will be discussed.

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Electronic Structure of Doped Fullerenes and Nanotubes

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We investigate the influence of n-type doping on the electronic structure of different fullerene systems and single wall carbon nanotubes. The influence of the doping is monitored by soft x-ray absorption, soft x-ray emission and resonant inelastic x-ray scattering, which allows us to detect changes in both the occupied and unoccupied electronic states in an atom specific manner, enabling us to selectively study either the carbon cage or the dopant. We present results for (a) single wall carbon nanotubes, which have been doped *interstitially* by K intercalation, (b) $\text{La}@C_{82}$, where La acts as an *endohedral* dopant and (c) $(C_{59}N)_2$, where the substitution of a C atom by a N atom in each C_{60} ball has been discussed as an *on-cage* doping situation. In a nutshell, we find (a) an enhanced density of states at the Fermi level on the carbon cage, (b) residual valence charge at the La atom indicating an incomplete charge transfer and the existence of hybridization and (c) the presence of the “doping” electron locally at the N site, in agreement with electronic structure calculations.

Topology of the Fermi surface and Band Structure near the Fermi level in the *Pb*-doped *Bi*₂*Sr*₂*CuO*_{6+δ} superconductor

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Recently, the resolution of the angle resolved photoemission spectroscopy *ARPES* have been significantly improved. A large number of the high resolution *ARPES* experiments have been performed on *Bi*₂*Sr*₂*CaCu*₂*O*_{8+δ} (*Bi*2212) and revealed many notable features of the band structure, such as the findings of one band crossing the Fermi level, a large Fermi Surface (*FS*) centered at (π , π) point in the First Brillouin Zone (*BZ*), extended Van Hove singularities near (π , 0) and a peak with a humped shape spectrum near (π , 0). However, it is still less clear whether all these detailed electronic structures revealed by *ARPES* are characteristic of all superconductors or very specific to *Bi*2212.

In order to make this clear, we have performed *ARPES* measurements on *Pb*-doped *Bi*₂*Sr*₂*CuO*_{6+δ} (*Bi*2201) superconductors with various doping levels by using very high angular and energy resolutions of 0.26 degree and 5 meV, respectively. The T_C values of the samples turned out to be OD_<2K, OD_6K, OD_24K, and UD_16K, where OD and UD stand for the doping level of the samples; over- and under-doped, respectively. The *ARPES* spectra were measured at temperatures 6-100 K with an incident photon energy of $h\nu = 21.218$ eV. The *Bi*2201 OD_<2K sample measured with $h\nu = 21.218$ eV shows a *FS* with an electron-like closed shape centered at Γ point, though *Bi*2212 always shows an open *FS* when it is measured with $h\nu = 22\text{eV}$ ^[1]. The *FS* of *Bi*2201 becomes open when the doping level is decreased. We calculated the area surrounded by the *FS* in the first *BZ*, which directly corresponds to the doping level of the sample. The doping dependence of the transition temperature T_C is discussed in comparison with those of *La*_{1-x}*Sr*_x*CuO*₄, *YBa*₂*Cu*₃*O*_{8-δ}, and *Bi*2212.

[1] H.Ding *et al.*, Phys.Rev.Lett., **78** 2628 (1997).

Spin Polarization and Dichroism in ARUPS from Thin Rare Earth Films

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In the present study, spin polarization and dichroism were investigated in angular resolved VUV and soft-x-ray photoemission from magnetized as well as paramagnetic rare earth surfaces. Thin Gd, Tb and Tb/Gd films exhibiting (0001) surfaces were prepared by MBE on W(110) and Mo(110) substrates. The photoelectrons were excited by polarized synchrotron radiation from the 6.5mNIM, PM-3 and U2 beamlines of the BESSY synchrotron radiation source, covering an energy range from 6eV to 1keV. A SPLEED detector attached to a single axis goniometer based electron spectrometer was used for angular resolved spin analysis. The main part of this work was focused on the characteristic surface state of the rare earth metals. The Gd surface state shows a splitting of about 20meV as been proved by linear magnetic dichroism and spin polarized photoemission. The spin analysis shows that the two observed states have opposite spin character. Temperature dependent measurements have been used to investigate the magnetic coupling of one monolayer of Tb adsorbed on a thin Gd(0001) film. The magnetic as well as the nonmagnetic circular dichroism observed from the Gd 5d surface state is compared to measurements taken from the 4d core level. The experimental findings will be compared to full relativistic single step photoemission calculations.

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Spectromicroscopy On Liquid Interfaces

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Wetting/dewetting and emulsification /phase separations in liquids are fairly common phenomena, although there detail investigation on microscopic level is still a challenge task. Traditional chemical techniques, such as IR, MR, Raman, often can not reach the spatial resolution needed. High-resolution microscopic techniques are limited, liquid interfaces can not be examined in vacuum (electron microscopy), and for AFM measurements tension/friction forces are too small and do not lead to a desirable contrast. Scanning Transmission x-ray Microscope (STXM) combines chemical sensitivity of x-ray absorption spectroscopy with high-resolution microscopy and is a unique and powerful tool for the spectroscopic analysis at the scale from 50 nm to tens of microns. In addition, as a photon in- photon out technique, it can be easy adopted for liquid-phase samples. Presented article includes the measurements of wetting properties of Si_3N_4 membrane by pure water and a dynamic of phase separation of PS/PDMS polymers, with additional emphasis on a role of clay as a compatibilizer. Liquid droplet in contact with a solid surface always assumes the shape, that gives the lowest total energy. At liquid/ vapor interface L/V, in the vicinity of solid S, it may exhibit a finite equilibrium contact angle (partial wetting) or a strictly vanishing contact angle (complete wetting). Contact angle (according to the Young equation) is determined by the interfacial tensions. In vertical direction, the equation is not balanced, so one need to consider a stress produced by liquid/gas interface on solid. Such stress may not be uniform (due to Poisson's relation) and leads to a difference in the contact angle, so one has a spreading in the contact angle value between "slipping" and "mesa" regime, as clearly seen in x-ray images even on an individual droplet. Due to a small penetration depth, a water layer as thin as 20 nm may be examined, and that allowed us to see the precursor film formation accompanied by a micro droplet movement. Because the tension coefficients are temperature dependent, the temperature T may exist, at which a finite contact angle is switched to a total wetting [1]. We found, that such transition can occur near the temperature of a water crystallization, so the transformation from completely wetted behavior to a drop formation was imaged on line. PS/PDMS system is a well know example of immiscible polymers, and in the absence of a clay produces a well define pattern, which shape and domain size depends also on the temperature. The later can be control in the experiment, and one can see a phase separation in real time of low molecular weight polymers. The addition of clay produces a homogeneous film on the scale of STXM resolution (50nm). Varying the amount of

clay, we had succeeded to see a shape bunching of individual droplet, and in this sense can derive the stress and the tension on the clay interface. We hope, that in such way we can determine is clay acts only as super grafts whereby the different type of polymers absorb to the large free surface, or a rigidity of clay platelets prevents large curvature and

Dichroism in Angular Resolved XPS from Gadolinium Core-level

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Magnetic dichroism in core-level photoelectron emission from solids represents a promising new element-specific probe of surface and interface atomic structure and magnetic order. This work reports on magnetic dichroism in angular resolved photoemission from the Gd 4l (l=s,p,d,f) core-levels of in-plane magnetized Gd films excited with linearly and circularly polarized, as well as unpolarized, light. Thin Gd films of about 100ML thickness were evaporated onto a W(110) substrate at room temperature, and subsequently annealed to 700K to form an ordered layer exhibiting a (0001) surface. The experiments were performed using polarized synchrotron radiation from the bending magnet beamline 9.3.2 at the Advanced Light Source in Berkeley or an unpolarized Al-Ka X-ray source. High resolution spectra were taken by means of the advanced photoelectron spectrometer-diffractometer (Scienta SES-200) end-station presently situated there. The dichroism measurements were performed by physically rotating the sample azimuth so as to change the direction of the magnetization axis relative to the incident light. The magnetic dichroism asymmetries were obtained by calculating the normalized difference between spectra obtained with the two mutually orthogonal orientations of the magnetization. Strong asymmetries were observed, even when exciting the spectra by means of unpolarized light. The experimental results are compared to 3-step photoemission cluster calculations based on a relativistic full potential algorithm including magnetic exchange and core multiplet effects.

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Temperature-dependent Angular Resolved UV-Photoemission Spectroscopy from CeNi_2Ge_2

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Pronounced temperature-effects in angular resolved ultraviolet photoelectron spectroscopy from the (001) surface of the ternary heavy fermion compound CeNi_2Ge_2 are presented. The measurements were performed on atomically clean and well-ordered thin films grown on a W(110) substrate. The spectra were excited by means of HeI (21.2eV) and NeI (16.8eV) light. A strongly enhanced intensity at the Fermi edge is observed at low temperatures for this excitation energy. The variation of the detection angle shows not only a variation of the intensity but also of the position of the signal near the Fermi edge. In addition, the intensity in the range of the Ni derived d-bands and the yield of the true secondary electrons increase. Finally, the work function is drastically raised with temperature, exhibiting an unusually high positive temperature coefficient of about 0.65meV/K. The observed temperature dependency hints on a strong redistribution of the states near the Fermi-energy with increasing temperature. A simple model will be presented that correlates the change of the work function with the density of states at the Fermi-energy and such is capable to explain the observed temperature dependency.

Support by the DFG (SfB 252, TP: F4) is gratefully acknowledged.

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Support by the DFG (SfB 252, TP: F4) is gratefully acknowledged.

Chemical Mapping Of Biological Objects.

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The chemical mapping of biological specimens requires a method which combines chemical sensitivity with high spatial resolution. This article presents our latest advances in the mapping of biological objects using the chemical sensitivity of X-ray Absorption Near Edge Spectroscopy (XANES). We present the first oxygen K edge spectral images of a frozen hydrated 3T3 cell and carbon K edge measurements of a dried bacterial culture.

The mouse 3T3 cell line was chosen as a typical mammalian cell. We followed the same freezing protocol of plunging in liquid ethane first developed for cyro-TEM measurements and found it reliable and reproducible for preserving of the cell's hydration state. The spectra of individual structures of the cell were measured by collecting a series of images at closely spaced steps in energy [1]. In this way, reliable spectroscopic information from features as small as the microscope's resolution can be extracted. For comparison, the spectra of different standards, such as DNA, small polypeptides, and amino acids were measured in the dry state. The images across the oxygen edge show moderate contrast, mostly associated with a density modulation inside the cell. The main distinguishing feature in the spectra, apart from the water absorption, is the peak at 532.35 eV. This peak is assigned to the $1s\text{-}\pi^*$ transition of the C=O bond which is common to all polypeptides.

For spectromicroscopy at energies above 536 eV, the thickness of the water layer plays a crucial role. Too thick water layer results in the rapid reduction of S/N ratio due to strong x-ray absorption, too thin water layer leads to dehydration and osmotic shock of the cell prior to cryo-fixation. We have examined this effect and clearly see the cell's outer membranes rupture if the preparation time exceeds 30 s.

The carbon edge spectroscopy was performed on *Pseudomonas* sp. Bacteria, used for heavy oil purification. Samples were taken at different stages of oil processing and small droplets of the water-oil emulsion were allowed to dry on Si_3N_4 windows. These samples were examined using a soft x-ray microscope scanning across the carbon edge. This allowed us to show that as a consequence of microbial action significant chemical changes occur not only in the composition of crude oil, but the bacteria also show significant chemical changes due to the accumulation of oil products within the cells. Spectroscopic analysis shows that the bacteria which participated in the reaction contain more aromatic and aliphatic compounds, as seen from the peak increases at 185.3 eV ($1s\text{-}1/\pi^*$ in the aromatic ring bonds) and at ~287 eV ($1s\text{-}3p_{\text{mixed}}$ with $1s\text{-}\delta^*$ in C-H bonds).

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Inner-Shell Absorption Spectroscopy Of Amino Acids.

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This work extends early experimental [1] and computational [2] studies of the near edge X-ray absorption (NEXAFS) spectra of amino acids and small polypeptides. Those studies demonstrated that NEXAFS spectroscopy can uniquely identify particular amino acids, thus providing a basis for chemical mapping in soft x-ray spectromicroscopy. Amino acids, which include an aromatic ring, were found to have distinct spectral features, and they do not change significantly during peptide bond formation. These species, along with sulfur containing amino acids, are likely the most suited for chemical mapping of polypeptides. Here we present significantly improved near C edge spectra of 20 common amino acids, and a detailed spectral interpretation based on ab initio computations. Initial comparisons of these improved results with the earlier calculations [2] revealed limitations of approximations used in that computational approach. This stimulated the development of a new method of static exchange (STEX) with polarized core. This helps to resolve a discrepancy between experiment and our previous computational simulations of the NEXAFS spectra for simple (aliphatic) amino acids and demonstrates the potential of STEX ab initio calculations to predict the NEXAFS spectrum of complicated molecules. It is well known that amino acids can form a different ion- state and in solution their de-/ protonation depends on pH. The ability of amino acids to take on such confirmation (zwitterion), with hydrogen atom of carboxyl group transferred to amino group, is essential for all chemical properties of amino acids. As a part of our investigation, we present NEXAFS spectra of Gly solutions with different pH. Contrary to the common assumption, that a proton exchange has a negligible influence on C edge NEXAFS spectra, experimental data clearly show the difference. Based on these measurements, we can identify the protonation ratio for the dried form of amino acids, which is not an equilibrium state, and so can not be measured on the basis of simple analytical chemistry. Qualitatively it is possible to correlate specific NEXAFS features with functional groups and in some cases, individual bonds, such that the total spectrum can be considered to be a linear combination of "elementary" spectra. This approach, named the "building block principle", provides a useful starting point in the interpretation of the spectra of very complicated molecules. However there are clearly limits to the building block approach. One theme of this work is to explore these limits in the case of peptide bond formation. As we show, conjugation (delocalization of electronic charge across multiple functional groups) leads to new molecular orbitals during polypeptide bond formation, combining the properties of the conjugated groups.

Orbital Ordering in strongly correlated materials studied by x-ray resonant diffraction: the case of LaMnO_3 and VO_3 .

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We reexamine the ground state properties of the Antiferromagnetic Insulating Phase of VO_3 in the light of the recent experimental observations by L. Paolasini et al [1] based on Resonant X-ray Scattering at the V K-edge and non-resonant magnetic scattering. We show that even in the case that the two magnetic electrons are coupled to spin $S = 1$, as experimentally found in ref. [1], it is possible to repeat the analysis performed by Castellani et al [2] on the basis of spin $S = 1/2$, leading again to an orbital degeneracy and consequently to an orbital ordering. In this case however the orbitals are to be intended as two-electron states. All this is born out by the study of the effective hamiltonian with spin $S = 1$ and pseudospin $\tau = 1$, derived in the atomic limit from a Hubbard model hamiltonian written for three bands and two electrons per site. We discuss also the possible origin of the resonant signal at the $(1,1,1)$ monoclinic reflection showing that to a very good approximation magnetic scattering can be ruled out and that a very plausible explanation is provided by the orbital ordering of the system (Templeton scattering). Indeed realistic calculations for the response function for non-magnetic resonant scattering based on the $3d$ charge distribution suggested by the above model show a very good agreement with the energy and azimuthal scans presented in ref. [1]. On the contrary we show that resonant x-ray diffraction at the Mn K-edge is not a suitable technique for the direct observation of orbital ordering in LaMnO_3 compound.

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[2] C. Castellani, C.R. Natoli and J. Ranninger, Phys. Rev. B 18, 4945 (1978)

Scanning tunneling microscopy as local probe of electron density and dynamics

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We report on novel approaches to measure the dynamics and potential landscape of surface electrons. The spatial decay of interference patterns in the local density of states for surface state electrons on Ag(111) and Cu(111) is used to determine quantitatively the phase relaxation length and femtosecond lifetime of the hot quasiparticles. The decay is governed by inelastic electron-electron scattering and we find a $(E - E_F)^{-2}$ energy dependence of the lifetimes for both Ag and Cu, and our values are comparable to the corresponding bulk electron lifetimes [1]. Direct potential imaging is based on the Hohenberg-Kohn theorem, which states that the ground state electron density completely determines the external potential acting on an electron system. The electron potential in surface systems can thus be mapped by applying linear response theory to the total electron density as measured with scanning tunneling microscopy. Direct potential imaging is demonstrated for the surface state on Au(111), where the herringbone reconstruction induces a periodic potential modulation [2].

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[2] L. Bürgi, H. Brune and K. Kern, to be published

Chemical Shifts in O-K edge ELNES/XANES of Oxides

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It is well known that surface oxide film or intergranular oxide film often governs the properties of functional and structural materials. "Chemical shift" in the O-K edge ELNES (Electron Energy Loss Near Edge Structures) or XANES (X-ray Absorption Near Edge Structures) is one of the valuable informations to understand the chemical bonding state in the oxides. However, energy of the O-K absorption edge of major metal-oxide crystals varies depending on species of cation element, although formal charge of oxygen ion is always 2-. Therefore, in the present study, first principles calculations are systematically conducted to clarify the origin of chemical shift in the ELNES/XANES from viewpoint electronic structure. Calculated chemical shifts of divalent-, trivalent- and quadrivalent-metal oxides in 3rd, 4th and 5th rows in the periodic table, which are common in ceramic materials, are analyzed. It is found that the chemical shift of oxides in 4th or 5th row in the periodic table agrees with the trend simply anticipated by difference in electronegativities between metal element and oxygen, except for SrO. The deviation from the trend in SrO is found to be ascribed to change of valence band structure. Comparing of electronic structures of oxides in the same row or in the same column in the periodic table, factors to determine the chemical shift are classified into a few features in electronic structure, which is valuable for the analyses of chemical shift of unknown materials.

X-ray Absorption and X-ray Photoelectron Spectroscopy in the Multi-Torr Pressure Regime: First Results for Solid and Liquid Water*

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We have performed NEXAFS and XPS investigations of the surface and the near-surface region (~0.5 micrometer) of ice and liquid water at temperatures in the range from 173 K to 274 K. A newly developed high-pressure NEXAFS and XPS apparatus uses windowed fluorescence detection for x-ray absorption and separates the high-pressure sample region from an electron spectrometer by a differentially-pumped transfer lens, permitting both measurements to be performed at elevated pressures. As a first application, this apparatus has permitted measuring ice and water samples in equilibrium with their vapor (e.g. at pressures of up to several torr). Our NEXAFS measurements reveal that the ratio of ordered (ice-like) vs. disordered (water-like) regions in our polycrystalline ice samples is increased when approaching the melting point. The large escape depth of fluorescent photons in ice/water (~0.5 micrometer) implies that the liquid-like layer is present throughout this depth range. This argument is supported by angle-of-incidence measurements. It is argued that, in addition to the liquid-like layer at the ice surface, there is also a liquid-like layer at the grain boundaries of the polycrystalline ice. Our high-pressure XPS measurements point to a new class of surface science investigations at pressures closer to those in many practical environments, and we will also discuss some future directions for research of this type.

XPS Investigations of Sandwich Structures of Cu-phthalocyanine Derivatives Deposited onto the Cu-phthalocyanine Surface

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X-ray photoelectron spectra (XPS) of samples of copper phthalocyanine (PcCu) pigments modified with different quantities of defloculating additives (DA) were measured. The investigation of sandwich structures was performed using ES-100 and XSAM-800 spectrometers. Investigations of the determination of the degree of filling of the Pc pigment surface by DAs and description of the modifying layer structure have been carried out.

We investigated the stable π -modification of the blue phthalocyanine pigment (PcPg). The substituted arylides of PcCu with different functional groups in phenyl nucleus were used as defloculants. Their general formula is $\text{PcCu}[\text{SO}_2\text{NHC}_6\text{H}_4\text{X}]_m$, where $\text{X} = \text{H}, \text{OH}, \text{SO}_3\text{H}, \text{OCH}_3$. For the first time XPS was used for quantitative determination of the number "m" of sulphonyl groups. Nitrogen atoms were used as a calibration standard. These atoms are contained both in PcCu and in different sulphonyl groups. Since the relative concentration of copper and nitrogen atoms in PcCu is 1:8, this ratio is 1:(8+m) in $\text{PcCu}(\text{SO}_2\text{NHC}_6\text{H}_4\text{X})_m$. Having knowledge of the ratio of integral intensity of lines $\text{N}1s$ to $\text{Cu}2p$, it's possible to determine an «increase» of the number of nitrogen atoms, i.e. the value m . The obtained results are correlated with the data of potentiometric titration and microanalyses. Since the sulphur is contained in DA only, while the copper is contained both in DA and in PcCu (with different atomic concentrations), we choose sulphur atoms as a calibration standard in the consequent experiments. It allows one to track the process of layer fill-up.

We determined that, for all modified samples, the amount of the modifying addend required to form a stable monolayer on the Pc pigment surface is about 10 mol.%. Relying on the experimental results obtained, the modification mechanism and the structure of modified upper surface layer were proposed. The DA-molecules were assumed to be fixed vertically at the PcPg surface (for first monolayer) and the functional groups of DA-molecules are inserted into interplanar space of PcPg crystal. Next layers were formed with vertical-horizontal orientation of monolayers. Theoretically calculated value of a surface occupied by DA-molecules coincides completely with experimental data.

High resolution ARPES study of the electronic Structure of CMR Oxides

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We have used angle-resolved photoemission (ARPES) to measure the electronic structure and Fermi Surface of cleaved single crystals of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ using greatly improved energy and momentum resolution. Similar to our earlier studies[1], we observe a spectral depletion or pseudogap at E_F . The greatly improved energy and momentum resolution of the new experiment now allows us to directly measure the real but very weak Fermi cutoff and to study the k-dependent details of these Fermi states. We find a locus of low-energy excitations that very closely matches the large Fermi Surfaces predicted by band theory[1], indicating a large number of carriers. However, we also find the very unusual result that these near- E_F states do not appear to be associated with a quasiparticle but are instead from an incoherent spectral function. This possibility of a Fermi Surface without quasiparticles may require a new paradigm for understanding strongly correlated electron systems. Similar but less dramatic effects may also be occurring in the underdoped cuprates.

[1] D.S. Dessau *et al.*, Phys. Rev. Lett. **81**, 192 (1998).□

Automated Angle-Resolved Photoemission with in situ MBE at KEK-PF BL-1C

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In order to investigate the electronic structure of quantum nanostructures, a VUV beamline with high-resolution and high-throughput photoemission spectrometer has been constructed at the BL-1C of the Photon Factory. For observing the electronic structures of quantum nanostructures such as quantum dots (0D), quantum wires (1D), ultrathin films and quantum wells (2D) and other low dimensional materials, photoemission experiments with high energy- and momentum-resolution are indispensable. It is also noted that the state of the art photoemission techniques such as Fermi surface mapping require an automated angle-scanning system.

For this purpose, an angle-resolved photoemission spectrometer with high energy and angular resolutions; VG Microtech ARUPS10, was installed at the KEK-PF BL-1C end-station. This spectrometer has an entrance lens, which allows $\pm 0.2^\circ \sim 2.0^\circ$ entrance angle for photoelectrons. The total energy resolution of 31 meV at the 60 eV of photon energy is achieved. For the automated angle-scanning photoemission the electron spectrometer with a two-axis goniometer can be rotated in vacuum by the computer-controlled stepping motors. This automated angle-scanning system opens the way to perform Fermi surface mapping, x-ray photoelectron diffraction (XPD), photoelectron holography, etc. much easier and faster.

Another distinctive feature of this spectrometer is that it is connected to a conventional molecular beam epitaxy (MBE) chamber in ultrahigh vacuum (UHV). MBE is one of the most powerful technique for fabricating quantum nanostructures. In this system, the MBE-grown samples can be transferred into the photoemission chamber without breaking UHV.

The high-resolution photoemission results of surface reconstructions for MBE-grown GaAs(001) will be presented.

New Horizons in Resonant Soft X-Ray Scattering on Complex Solids and Macromolecules

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Generally x-ray scattering as used in structural studies is insensitive to details of the valence electron charge and spin densities. For example atoms in solids which differ in only the orientation of the electrical quadrupole moments because of differing occupations of valence orbitals are generally not distinguishable in conventional diffraction experiments

and are called crystallographically identical. At a core to valence resonant energy however the scattering cross section becomes strongly dependent on the details of the valence electron charge distribution as well as the spin distribution making these so-called identical atoms

distinguishable. Also the inelastic scattering at resonance allows for a study and identification of elementary excitations such as excitons and magnons and because of the short wave length allows for a momentum dependent measurement of their energies. In this talk I will present the basic physics principles on which these methods are founded and describe some recent results displaying the power of resonant soft x-ray scattering including a discussion of why these results are important. I will then speculate on a number of possibly very important new applications involving complex materials such as the high Tc superconductors, colossal magneto resistance materials, as well as macromolecular systems.

Electronic Structure of the Clean and Ag Covered Si(5 5 12) Surface

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The clean Si(5 5 12)-2x1 surface forms a single domain of row-like structures, providing a unique template for the growth of 1-D nanostructures. Our recent scanning tunneling microscopy (STM) studies show that noble metals such as Ag deposited and annealed on Si(5 5 12) indeed form a wide variety of well-ordered overlayer rows. We have used STM and synchrotron radiation photoemission to determine the surface and electronic structure of both the clean and Ag-covered (5 5 12) surface. Despite the many atomic substructures present in the clean 2x1 reconstruction, several distinct Si-2p surface core-levels and valence band surface-states are observed. The nature of these states is similar to those of clean Si(100)-(2x1), suggesting that they are derived from dimer/tetramer subunits. Scanning tunneling spectroscopy results indicate distinctive IV curves for the two main types of rows on the surface (tetramer rows and pi-chains). When low coverages of Ag (< 0.3 ML) are deposited onto Si(5 5 12) and moderately annealed ($T < 500\text{C}$), our STM studies show that Ag forms long monoatomic rows which nucleate along the underlying Si tetramer rows. Scanning tunneling spectroscopy (STS) data indicate that these Ag wires have a finite density of states at zero volts, indicating metallic behavior. For coverages between 0.3 ML and 0.5 ML, Ag forms sawtooth rows which evolve with coverage to an extremely well-ordered array of stepped double rows. We are presently correlating the STS results for this system with PES data taken at comparable coverages and temperatures. At higher coverages above 0.5 ML, both techniques indicate increasing metallicity of the surface.

Optical , Electrical and Transport Properties of Tris-8-Hydroxyquinoline

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Tris-8-Hydroxyquinoline (Alq) has been the subject of much interest due to its use as an electron transport layer and a light emissive layer in organic light emitting devices (OLEDs). Carrier injection and transport properties are of great importance in determining device performance and lifetime. We present a model for the current-voltage (I-V) characteristics of an OLED. We correlate this with measured I-V and electroluminescence characteristics of working OLEDs. We have also measured the chemistry and bonding structure of these OLED films using synchrotron radiation-based spectroscopy. The consequences of these results are discussed in the context of OLED performance and lifetime.

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A New Instrument for Angle Dependent XPS Studies

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Angle dependent XPS offers the ability to determine relative distributions, compositions and layer thickness for layers thinner than the XPS analysis depth. In practice, the use of angle dependent XPS is limited by the need to acquire data at several angles, usually requiring the sample to be tilted. The analysis of small features is also difficult because tilting the sample changes the analysis area as the projected shapes of the X-ray spot and / or analysis area on the sample change.

This instrument is based on an existing instrument where the electron input lens can be used to sequentially define two angles – a surface sensitive angle and a bulk sensitive angle, allowing angle dependent XPS without moving the sample. This method has now been extended to allow simultaneous collection of angle dependent XPS data from a range of angles.

In this paper, we describe this instrument present data from this instrument which shows the application to oxide thickness measurements and more complex structures.

New angle-resolved photoemission data on Bi₂Sr₂CaCu₂O₈ and Bi₂Sr₂CuO₆

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New high energy/momentum resolution Angle-Resolved Photoemission (ARPES) data on overdoped Bi₂Sr₂CaCu₂O₈ and Bi₂Sr₂CuO₆ will be presented.

Electronic structure of Nd_{1.85}Ce_{0.15}CuO₄: The view from photoemission

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The high-temperature superconductors are known to be doped antiferromagnetic insulators. The symmetry, or lack thereof, between doping with electrons (n-type) or holes (p-type) has important theoretical implications as most existing models implicitly assume symmetry. Most of what we know about these superconductors comes from experiments on p-type materials. The comparatively fewer experiments on the n-types suggest that there is a substantial difference between these two sides of the phase diagram. Despite this, the issue of electron/hole symmetry has not been seriously discussed, perhaps because the existing database is rather limited. We report a high-resolution angle-resolved photoemission spectroscopic (ARPES) study of the n-type superconductor Nd_{1.85}Ce_{0.15}CuO₄, the results of which contrast strongly with the p-type. The locus in momentum space of low lying excitations suggests a Fermi surface that is close to the LDA prediction. However, this "single piece" Fermi surface appears to derive from two distinct components in the low energy electronic structure, which dominate the spectra differently near $(\pi/2, \pi/2)$ and $(\pi, 0.2\pi)$. The larger feature disperses rapidly to higher energy as one moves towards $(\pi, 0)$ from $(\pi/2, \pi/2)$ in a fashion that resembles the d-wave like dispersion seen in the valence band of the undoped insulator. This is anomalous as a naive picture would put this valence band derived feature well below E_f with the chemical potential in the conduction band. Moreover, we find a very weak signature of the superconducting gap which is in contrast to the large anisotropic leading edge gap found in the hole doped systems. This confirms the fragile nature of superconductivity in this material.

Fermi Surface, Surface States, and Surface Reconstruction in Sr_2RuO_4

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The electronic structure of Sr_2RuO_4 is investigated in detail by high-resolution angle resolved photoemission spectroscopy (ARPES). We address the controversial issues of the Fermi surface (FS) topology and of the van Hove singularity at the M point, showing that a surface state and the replica of the primary FS are responsible for previous conflicting interpretations. In particular, by varying the incident photon energy and the temperature at which the samples were cleaved, we prove the surface state nature of the near- E_F peak detected at the M point. The relation of this state to a possible ferromagnetism of the surface is discussed. Furthermore, we identify an additional dispersive feature related to the electronlike γ pocket that had so far escaped detection in photoemission. A complete understanding of the data can be achieved only by recognizing that a $\sqrt{2}\times\sqrt{2}$ surface reconstruction takes place on cleaved Sr_2RuO_4 (as confirmed by LEED). This results in the folding of the primary electronic structure that, in turn, is responsible for the detection of shadow bands in the ARPES spectra. Taking these findings into account, the FS determined by ARPES is consistent with the de Haas-van Alphen results. In addition, ARPES provides detailed information on the shape of the FS and, in particular, direct evidence for the nested topology of the α and β pockets.

Epitaxial growth and the electronic structure of MgSe on ZnSe/GaAs (001).

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Mg based compounds are used in cladding and waveguide layers in wide band-gap light emitters. MgSe as a pure material has the NaCl structure but will grow with a zinc blende structure on zinc blende substrates. We have examined the growth and electronic properties of thin layers of MgSe grown on relaxed 0.6 micron thick ZnSe epilayers. This avoids potential complications when MgSe is grown directly on GaAs substrates.

Using relatively low energy photons from the BESSY1 synchrotron radiation facility to enhance the photoemission cross-sections, we have monitored the evolution of the 3d core levels of Zn, Se and Ga together with the 2s and 2p levels of Mg as a function of MgSe layer thickness, using the technique of angle resolved photoemission. By using a substrate temperature of 3500C, we obtained consistently good c(2x2) LEED patterns after each evaporation cycle: the maximum MgSe thickness investigated was 3.2 nm

From an examination of the energy shift of the Se 3d level following MgSe deposition (attributed to band bending) and determination of the apparent shift in the position of the valence band maximum, we estimate the true value of the valence band offset as -0.34 eV (relative to ZnSe).

Both surface and "bulk" Se contributions have been identified and an estimate of 0.44 nm for the inelastic mean-free-path of 56eV electrons in MgSe has been derived.

Normal emission valence band data utilizing a wide range of photon energies has been used to determine the band structure of MgSe (001) for the first time using the usual assumptions associated with a free electron final state model. Using an inner potential of 9.1eV we find the binding energies of the X5 and X3 points to be 1.5 eV and 4.0 eV respectively.

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Final-state effects in inelastic x-ray scattering: Resonant and Non-Resonant*

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In many inelastic x-ray scattering experiments, the final state of the system has an excitation of the valence electrons. In the simplest cases, the excitation is an electron promotion, producing an electron-hole pair or valence exciton. The role of electron-hole interactions in the final state has largely remained unaddressed, and we consider it here.

In ordinary inelastic x-ray scattering (IXS), a hard x-ray scatters inelastically, and measurement of the double-differential scattering cross-section permits one to probe a solid's dynamic structure factor $S(q,E)$ and dielectric properties. For low-energy losses, one probes inter-band transitions, the electron-hole continuum, and plasmon excitations. We will present ab initio results [1] for $S(q,E)$ for diamond and LiF, and compare them to measurements that probe the band-gap, excitons and plasmons. The indirect band gap in diamond is clearly seen.

In resonant inelastic x-ray scattering (RIXS) from cubic boron nitride (cBN) [2] and hexagon boron nitride (hBN) [3], a B 1s electron is excited into unoccupied energy bands by an incident x-ray. X-rays produced by radiative recombination of the core hole and valence electrons are detected. Thus, in the final state of the system, one has a conduction-band electron and valence-band hole (or a valence exciton). Minami and Nasu [4] considered the role of core-hole-exciton effects in the intermediate state and valence-hole-exciton effects in the final state in model calculations. We will present ab initio results for the role of both effects in cBN and discuss the effects in hBN.

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* This theoretical work was done in collaboration with experimental colleagues, W. A. Caliebe (BNL), C.-C. Kao (BNL), and K. Hamalainen (U. Helsinki), T.A. Callcott (U. Tenn.), D.L. Ederer (Tulane U.), L.J. Terminello (LLNL), and R.C.C. Perera (LBNL).

XPS-studies of structure transformations and relaxation processes in transition metal melts

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The absolute majority of commercial metallic alloys is produced by the smelting. In order to find the best way of the doping in the course of the smelting process, a more detailed knowledge of the chemical structure and the relaxation processes in metallic melts is necessary. The studies of the origin of the oscillatory character in time of the physical properties of allous require the measurements of the isothermal changes in the chemical structure of melts. One of such methods is the X-ray photoelectron spectroscopy - the direct method of investigation of the electronic structure of the matter. To obtain the data about the nature of relaxation processes in the transition-metal-based melts, one should study the dependences of these relaxation processes on the type and percentage of the doping elements and metalloids, as well as on the temperature of the melt. The unique X-ray magnetic photoelectron spectrometer for the investigation of melts is designed and constructed by us specially to solve these problems.

X-ray photoelectron studies of spin state changes in 3d-metal systems

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Fe₆₅Ni₃₅ magnetic alloy are known as the invar alloy. It means that these alloys have a low coefficient of the thermal expansion, which is increased only at the temperatures close to the Curie temperature for the ferromagnets. It is supposed that the enhancement of the thermal expansion coefficient is due to the changes of the magnetic moments of Fe and Ni atoms. In order to make clear of the problem, the electron structure, chemical bonding and the nearest neighbours of Fe and Ni atoms were investigated as dependent on the temperature. The 3s, 3p and 2p core level spectra and the valence band spectra were obtained. The changes of the spectra shapes of the valence bands and the core levels were observed at the transition of Fe₆₅Ni₃₅ alloy from ferromagnetic state to the paramagnetic one. This suggests the changes in the local environments of component atoms, their chemical bonds and the number of the unpaired 3d-electrons of the alloy components.

XPS-studies of the electronic structure of Fe-X (X = Al, Si, P, Ge, Sn) systems

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The investigations of the electronic structure of a number of iron-metalloid systems are carried out experimentally by the X-ray photoelectron spectroscopy (XPS) method and theoretically by the full-potential linear maffin-tin-orbital (FP-LMTO, TB-LMTO-ASA) method.

If the p-d-hybridization in the systems studied is considerable, the features of p-electron density of states (DOS) of the metalloid reveal themselves in the XPS valence band spectra, which reflect usually the d-electron DOS of a transition metal. In other words, the structure of the alloy valence band is formed similar to the structure of the valence band of the second component having more spatial extended valence electron charge distribution.

It is shown that the hybridization degree of 3d-electrons of iron and p-electrons of the metalloid is changed in dependence on the filling of the p-shell. In particular, the hybridization is increased in the following series of metalloids X= C, , P, Si, Al in Fe₃X – FeX systems.

Employing the metalloid atoms X belonging to the same IV-th group of the Periodic Table, namely, Si, Ge, Sn, which have the identical valence electronic configuration, we found that the shapes of XPS valence band spectra of the corresponding compounds Fe-X are very similar except for the widths of the spectra. With the increase of the atomic radius of IVth group metalloid the p-d hybridization in its compound with iron is also decreased

L-edge X-ray Absorption Spectroscopy of Biological Nickels: Oxidation States and Spin States

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L-edge X-ray absorption spectroscopy has been used to study the oxidation and spin states of biological Ni inside Ni-Fe hydrogenases and CO dehydrogenases in various enzymatic forms and under a variety of reaction conditions (such as the oxidized versus the reduced). The status of the enzyme films used for the L-edge measurements was monitored by FT-IR spectroscopy. The L-edge spectra were also measured under various experimental conditions: on bare sapphire, capped before cooling down and sealed behind silicon nitride window, to eliminate the possibility of vacuum interaction with our samples. These L-edge spectra were interpreted by ligand field multiplet simulations and by comparison with data for Ni model complexes. The spectrum for Ni in the native *D. gigas* ('form A') is consistent with a very covalent Ni(III) species. In contrast, most of the reduced hydrogenase samples exhibited high spin Ni(II) spectra. The spectra for hydrogenases and for CODH enzymes were also compared with each other. Ni L-edge absorption spectroscopy is a unique method to resolve the oxidation states and spin states of various biological nickels.